Volume of Oxide Vacancies in Fluorite and Perovskite Structured Oxides

Mogensen, Mogens Bjerg; Norby, Poul; Chatzichristodoulou, Christodoulos; Hendriksen, Peter Vang

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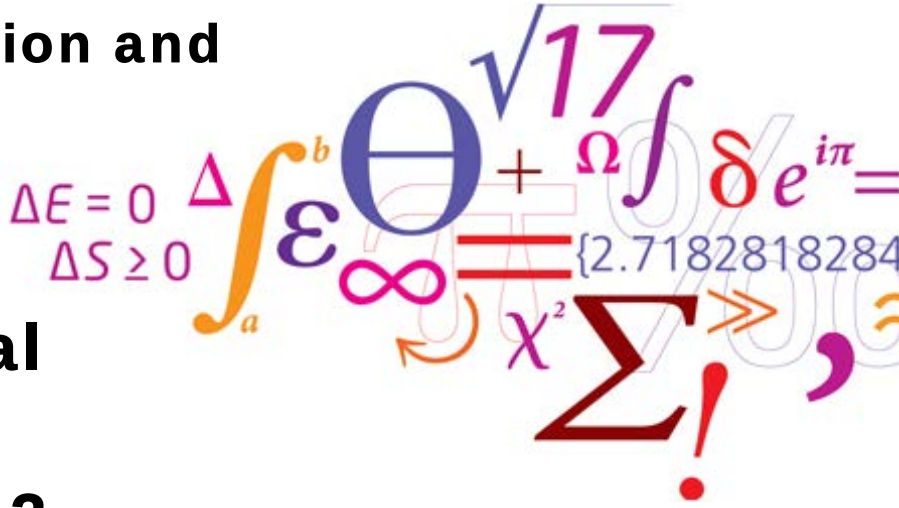
Mogens B. Mogensen, Poul Norby, Christodoulos Chatzichristodoulou, Peter V. Hendriksen

Department of Energy Conversion and Storage



Arthur S. Nowick Memorial Symposium

Kyoto, Japan, June 7, 2013

DTU Energy Conversion
Department of Energy Conversion and Storage

Introduction

Even though I never got to know Prof. Nowick, I know that some of his deep interests were properties of fast ion conductors and defect chemistry in general

I also know that he was Harry Tuller's PhD supervisor. Apart from all Prof. Nowick's own seminal scientific contributions, the contribution of educating Harry was - as time has proven – another great contribution to the science of ionic and mixed ceramic conductors

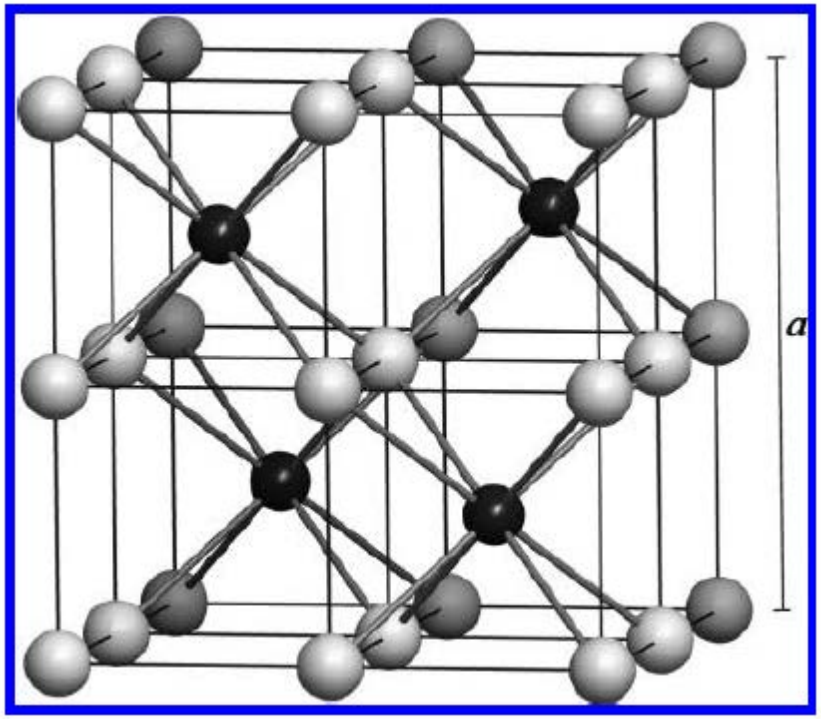
We will in the following minutes discuss about such materials and the volume of defects, i.e. the volume of oxide vacancies, inside them in memory of Prof. Arthur S. Nowick

Why is volume of vacancies interesting?

Some reasons are the observations that:

- **the crystal lattice shrinks if a fluorite like CeO_2 is doped with a 2 or 3-valent cation of approximately the same size as Ce^{4+}**
- **the induced ionic conductivity reaches its maximum as a function of dopant radius for the radius that does not change the lattice parameter of the host crystalline compound**
- **or expressed differently: The highest conductivity occur if Vegard's slope is zero**
- **or the conductivity - for a given dopant concentration - is highest in the stress free lattice**

Lattice constant empirical relations of doped fluorites



Empirical (Kim 1989):

$$a = a_0 + (A \cdot \Delta r_{cat} + B \cdot \Delta z_{cat}) \cdot x$$

Vacancies (Hong and Virkar 1995, Tuller et al 2012):

$$a = \frac{4}{\sqrt{3}}\left(r_{cat} + r_{an}\right)$$

$$r_{cat} = \left(1 - x\right) \cdot r_h + x \cdot r_s$$

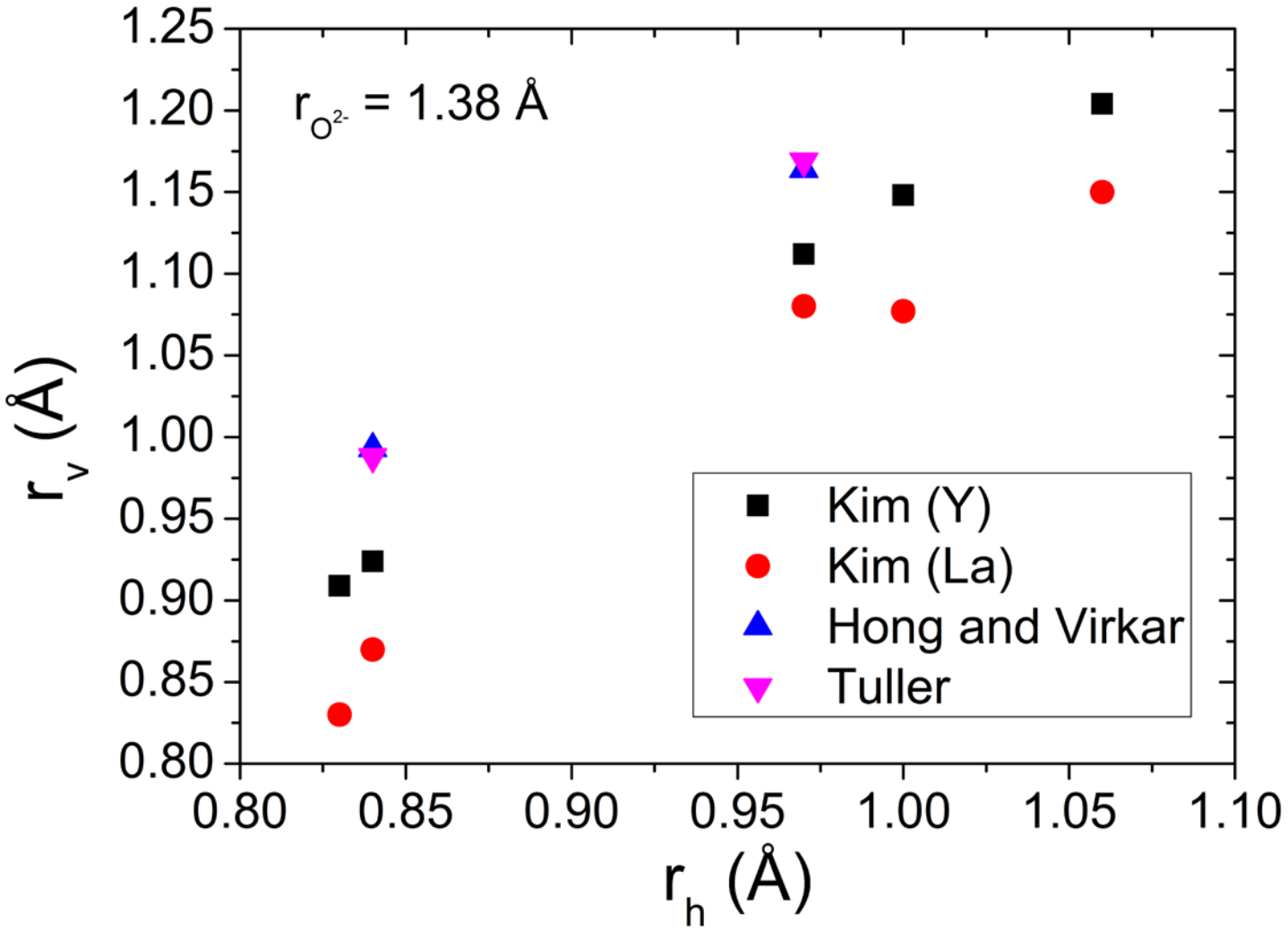
$$r_{an} = \left(\frac{2 - x/2}{2}\right) \cdot r_O + \left(\frac{x/2}{2}\right) \cdot r_V$$

Estimation of the oxide ion vacancy radius

r_v (Å)					
Compound	Ref.	Kim		Hong+Virkar	Tuller
HfO_2		0.999-0.484·Δr	0.909 (Y) (0.830 (La))		
ZrO_2		0.982-0.328·Δr	0.924 (Y) (0.870 (La))	0.993	0.988
CeO_2		1.120-0.189·Δr	1.112 (Y) 1.080 (La)	1.164	1.169
UO_2		1.155-0.432·Δr	1.148 (Y) 1.077 (La)		
ThO_2		1.189-0.328·Δr	1.204 (Y) 1.150 (La)		

$$r_v = r_O - \sqrt{3} \cdot B - (4 - \sqrt{3} \cdot A) \cdot \Delta r_{cat}$$

Dependence of oxide ion vacancy radius on host size



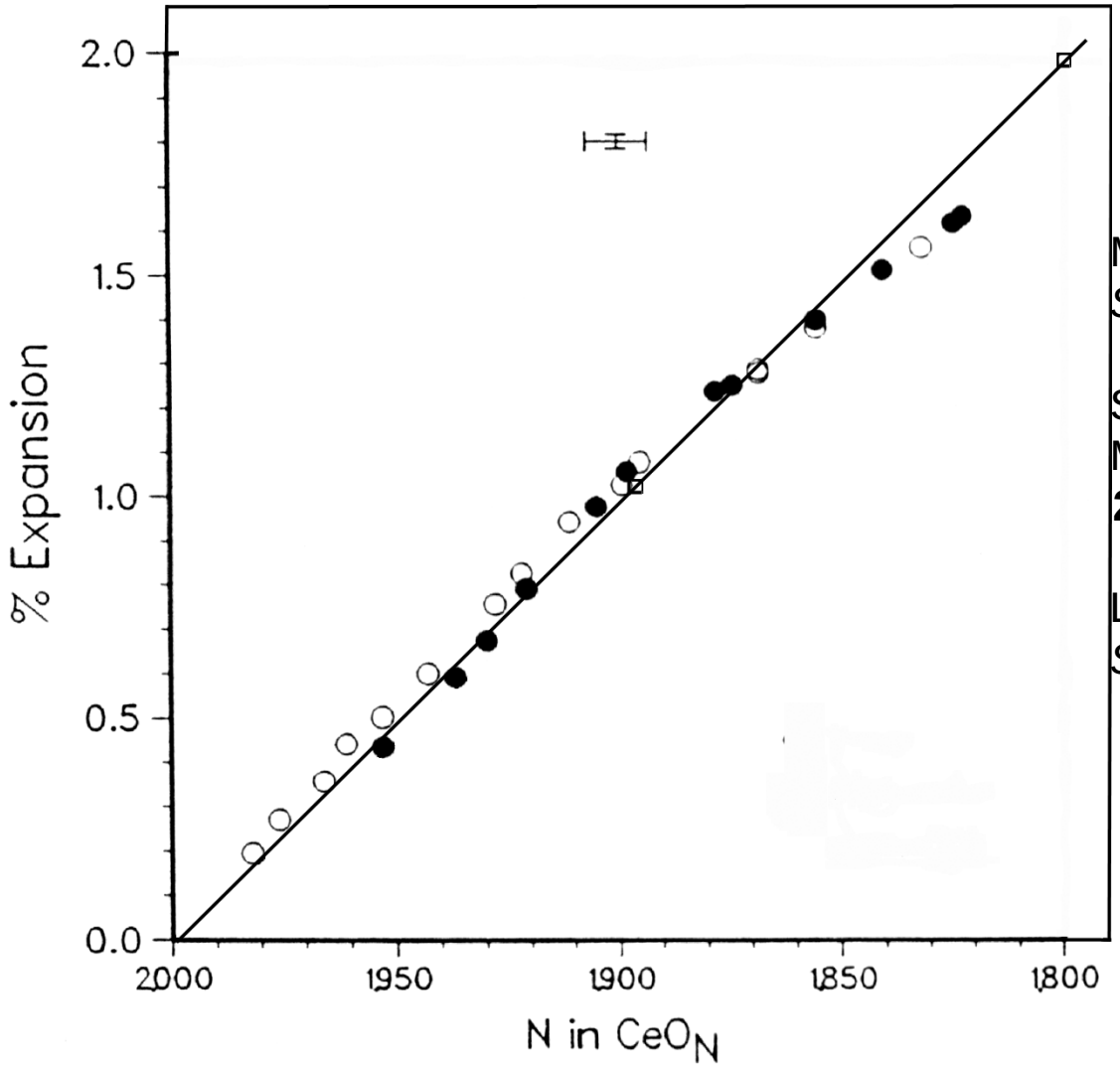
The weaker metal-oxygen bond the larger is the vacancy volume

Estimation of (3+)cation matching radius

r_c (Å)				
system	Ref.	Kim	Hong+Virkar	Tuller
HfO_2		0.938		
ZrO_2		0.948	0.937	0.938
CeO_2		1.038	1.024	1.024
UO_2		1.063		
ThO_2		1.112		

$$r_c = r_h + \frac{B}{A}$$

Expansion on reduction of ceria



Main data: Chiang *et al*. *Solid State Ionics*, **66** (1993) 85–95

Squares:G. Mogensen, M. Mogensen, *Thermochim. Acta*, **214** (1993) 47–50;

Line: best fit: M. Mogensen et al., *Solid State Ionics*, **129** (2000) 63

Stoichiometry expansion coefficients

Stoichiometry expansion coefficient, α_S, defined by:

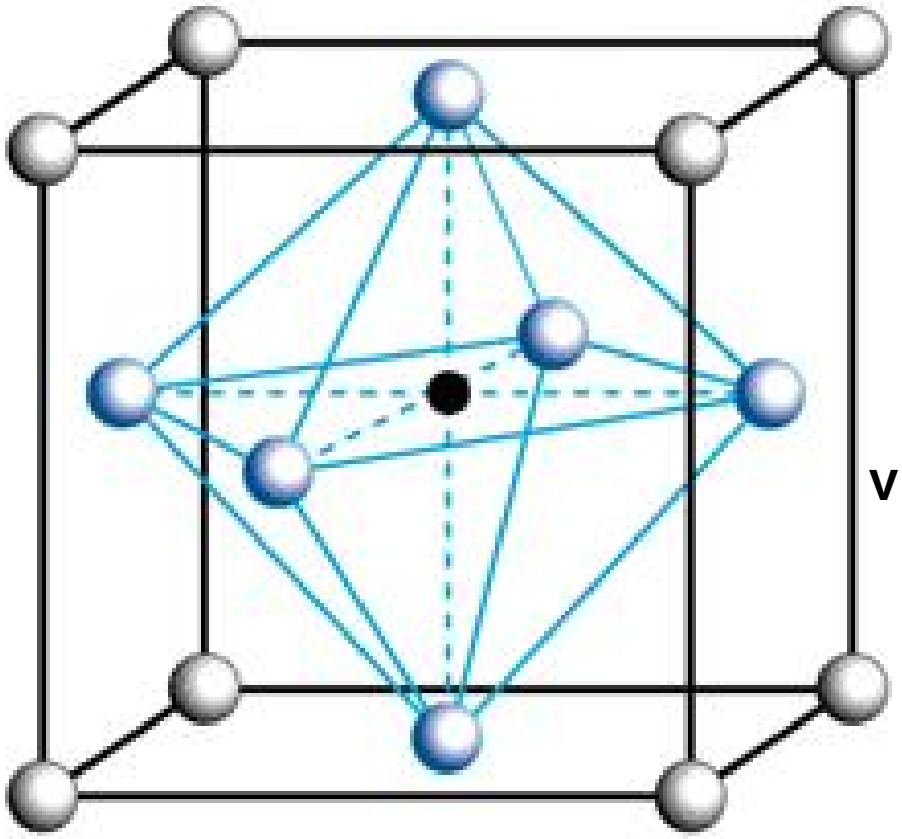
$$\varepsilon = \Delta L / L = \alpha_S \cdot \delta$$

where ε is the measured expansion, L is sample length, and ΔL is the change due to a change in oxygen stoichiometry of δ e.g. in reduced $CeO_{2-\delta}$ or in doped $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$.

P.V. Hendriksen et al., "Electrical conductivity and dimensional stability of co-doped lanthanum chromites", In: *Ionic and mixed conducting ceramics V*; eds. T.A. Ramanarayanan et al. Electrochemical Society Proc. Vol. PV 2004-25, 2008. p. 349-367.

α_S is about in the range of 2.3 – 3 % / vacant O for reduction of various doped $LaCrO_3$ and typically about 11 % / vacant O for reduction of ceria

Perovskite



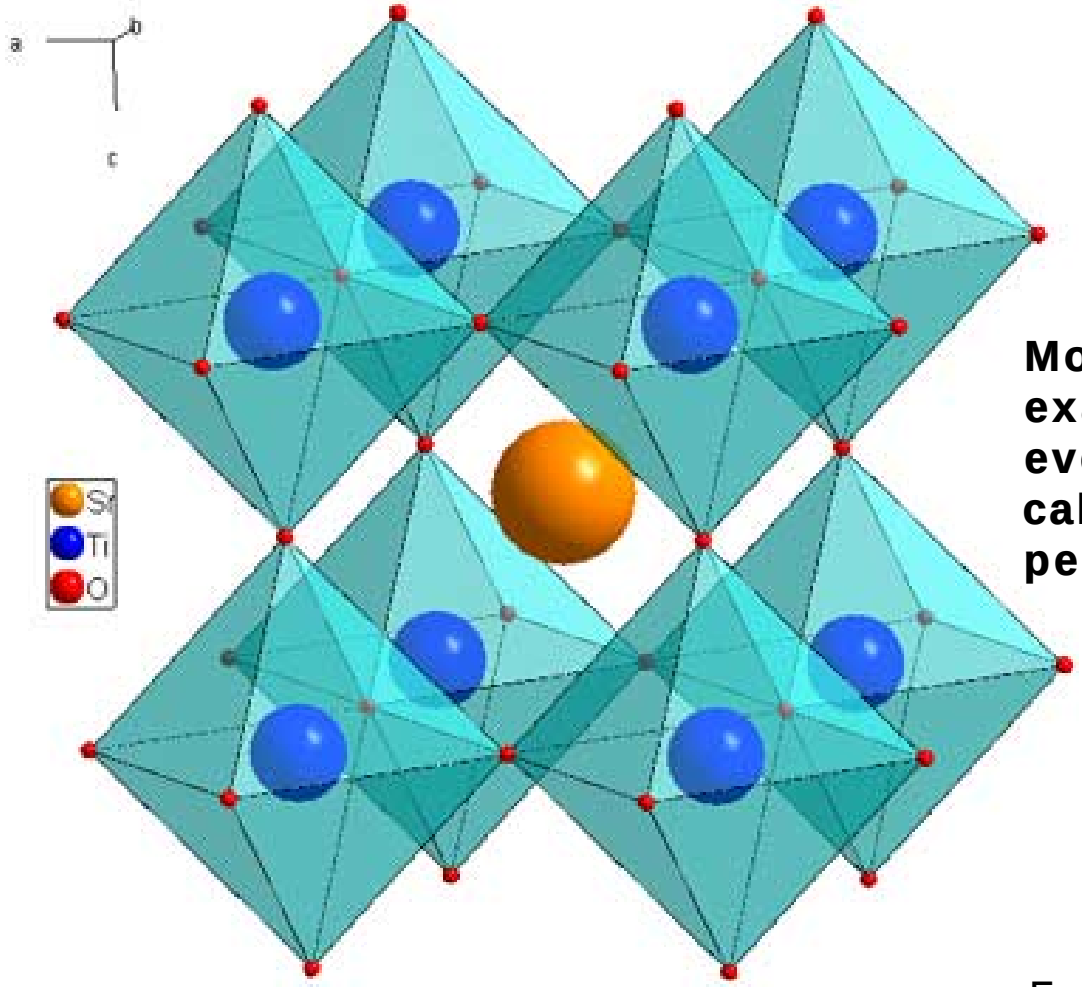
After V. P. Dravid

The O + A ions form together a cubic <u>closest</u> packed structure if the size of the A-ion is close to the size of the oxide ion.

Very strong B-metal-oxygen bonds

Perovskite structure (Grey atoms: A, Black: B, Blue: O)

Perovskite – a very flexible stucture



$SrTiO_3$

Most perovskites are not exactly cubic – and thus it is even more controversial to calculate vacancy volume in perovskites

From Cava Lab (J.R. Cava)

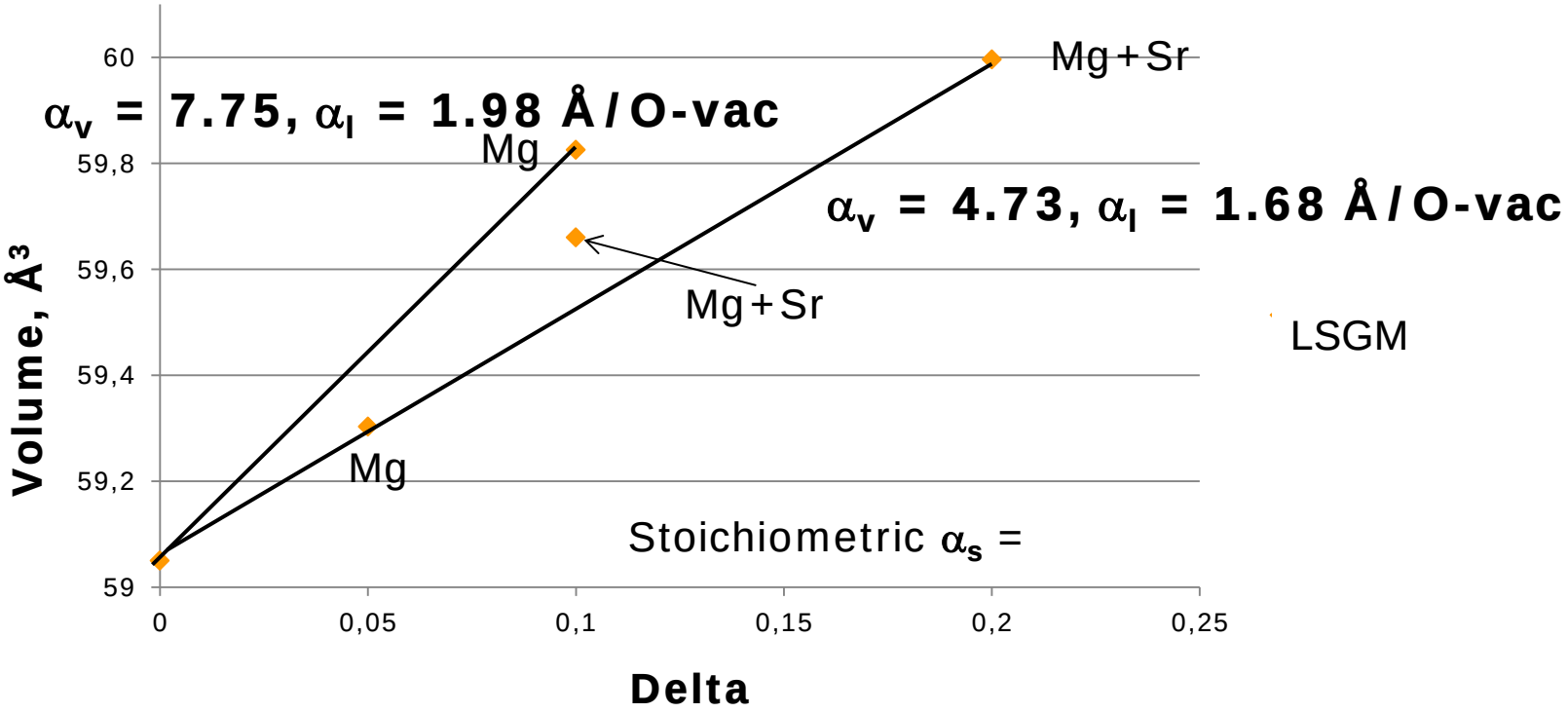
”Ideal” perovskite data

- r_{O2-} = 1.40 Å
- $r_{A,ideal}$ = 1.40 Å
- $r_{B,ideal}$ = 0.58 Å

- a = 3.96 Å

- V = 62.1 $Å^3$

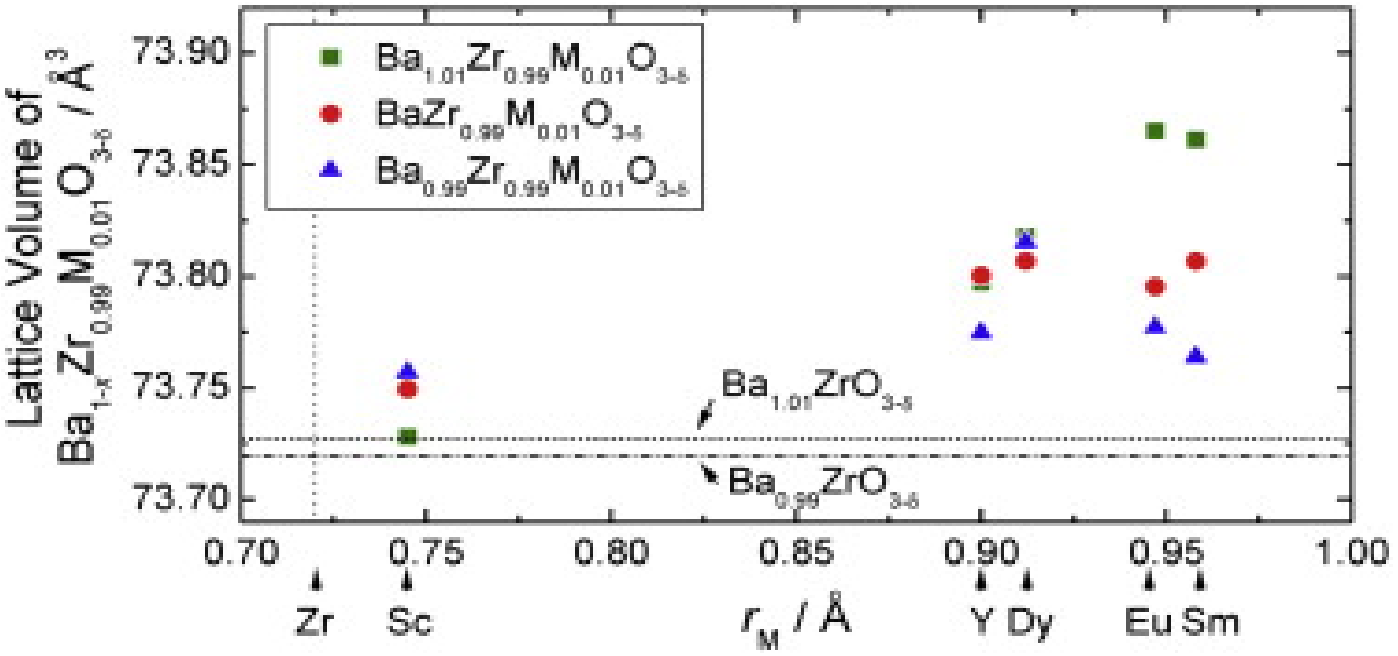
$La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-delta}$



Volume per formula unit versus oxygen sub-stoichiometry

Data from: M. Kajitani et al. *Chem. Mater.* 2003**, 15**, 3468 and 2005**, 17**, 4235 (neutron diffraction)

$BaZrO_3$



From: Donglin Han, Yoshitaro Nose, Kozo Shinoda, Tetsuya Uda
Solid State Ionics, **213** (2012) 2–7

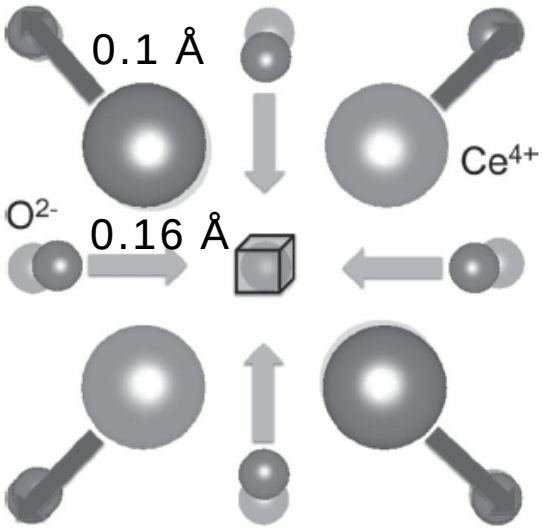
r_{Ba} = 1.61 Å

Introduction of OH^- (r = 1.37 Å) increases the unit cell volume with ≈ ½ - 1 %, i.e. r_v < 1.37 Å < r_{O2-} =1.40 Å

Conclusion

- Introduction of oxide vacancy without introducing cations bigger than the corresponding host shrinks the unit cell volume in fluorite and perovskite structured metal oxides
- In fluorites r_v increase with decreasing metal – oxygen bond strength
- In perovskites the situation is more complicated, but due to the strong B-ion-oxygen bond the volume changes tend to be less than half of what is typically seen in fluorites

Lattice shrinking contribution of vacancies



Tuller et al 2012

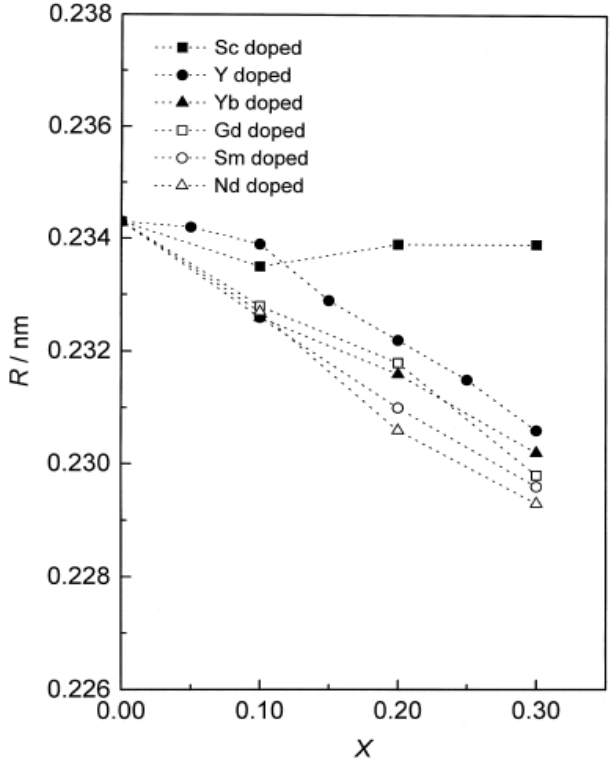


Fig. 4. The Ce–O inter-atomic distances in $Ce_{1-x}Ln_xO_{2-x/2}$ as a function of Ln content (Ln=Sc, Yb, Y, Gd, Sm and Nd).

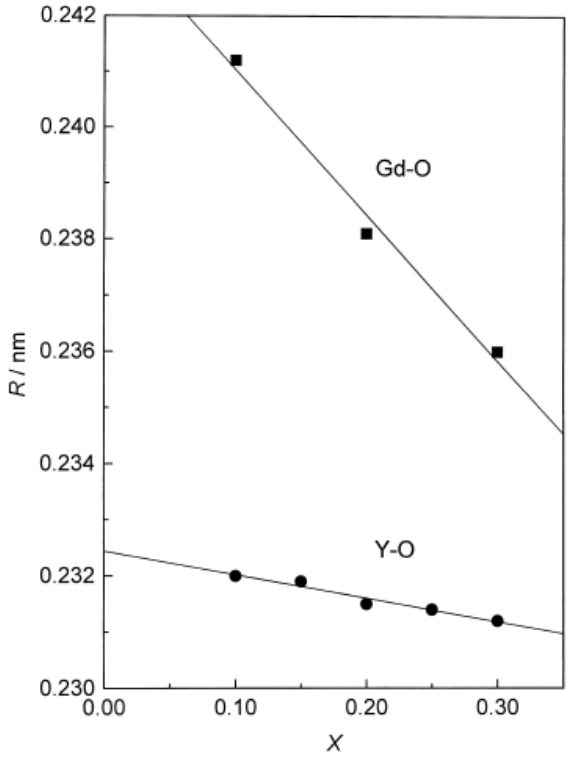


Fig. 5. The Ln–O inter-atomic distances in $Ce_{1-x}Ln_xO_{2-x/2}$ as a function of Ln content (Ln=Y and Gd).

Yamazaki et al 2000

- EXAFS results (and computational simulations) support this relaxation pattern
- This means though that the local volume at a vacant oxide ion site is actually increasing!

Model assumptions and limitations

- The cations have a coordination number less than 8 when the fluorite structure is acceptor doped and has vacancies, which affects their effective ionic radii. This difficulty is somewhat overcome by treating the vacancy as a species in the lattice possessing a certain radius.

- The oxygen vacancy radius is taken to be independent of concentration and dopant type.

- These calculations assume random distribution of the oxygen vacancies (and the dopant) and adopt a linear relationship between lattice parameter and dopant concentration (Vegard's law). Neither of these assumptions is true at higher dopant concentrations.

- The value of r_v does not represent the local structural modifications in the neighborhood of an oxide ion vacancy, but stems from the average lattice constant and acts as a parameter that includes all the structural complexity that is not accounted for by the model.

More precise model by Nakamura 2010

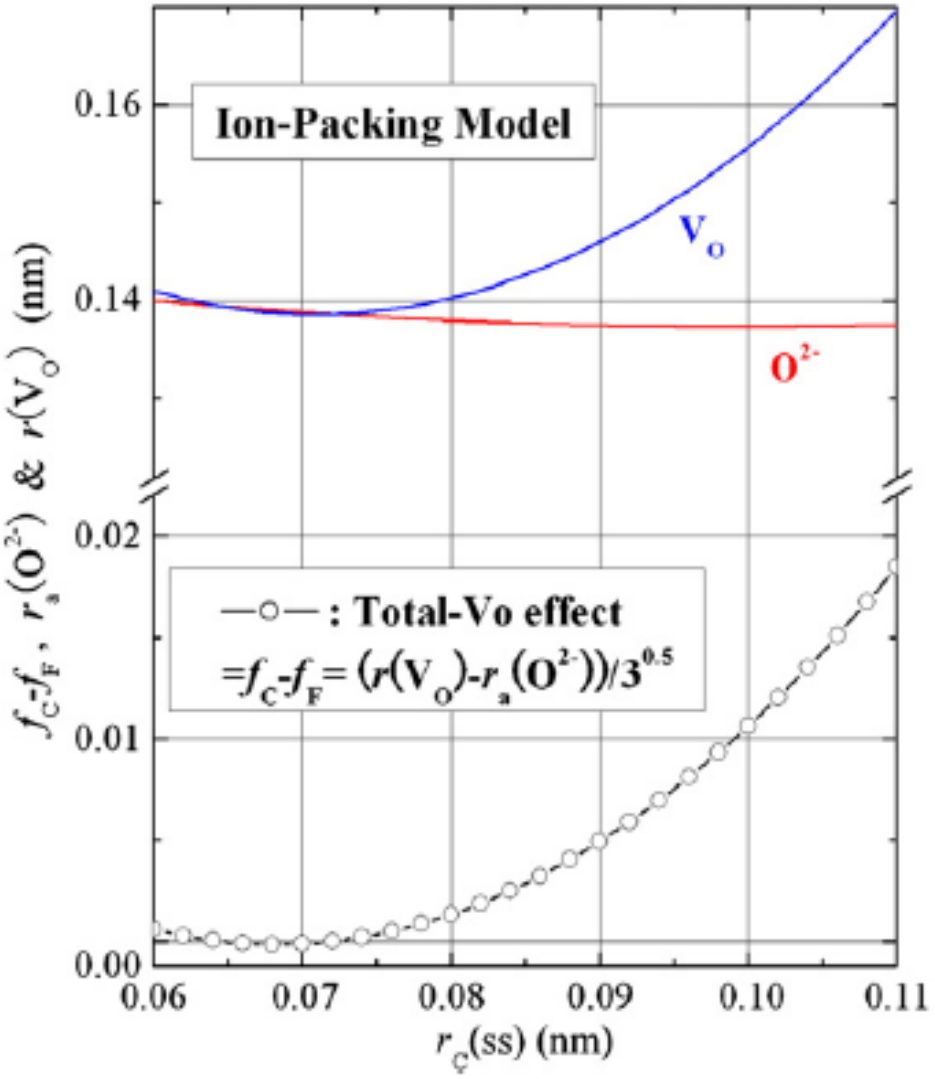


Fig. 10. $r_a(O^{2-})$ (Eq. (23)), $r(V_O)$ (Eq. (24)) and $(f_C - f_F)$ (the total V_O effect in Eq. (22)) curves as a functional of r_C(ss) in the present Ion-Packing (I-P) model.